

Magnetic susceptibility monitoring and modelling (MSMM)

Riley, Michael; Suttie, Neil; Stevenson, Carl; Tellam, John

DOI:

[10.1016/j.colsurfa.2018.12.003](https://doi.org/10.1016/j.colsurfa.2018.12.003)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Riley, M, Suttie, N, Stevenson, C & Tellam, J 2019, 'Magnetic susceptibility monitoring and modelling (MSMM): a non-invasive method for acquiring and modelling exceptionally large datasets from column experiments with manufactured nanoparticles', *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 563, pp. 289-301. <https://doi.org/10.1016/j.colsurfa.2018.12.003>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

Checked for eligibility 03/12/2018

Published in *Colloids and Surfaces A: Physicochemical and Engineering Aspects* on 04/12/2018

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

~~Evaluating quantitative models of manufactured nanoparticle migration processes in porous media using non-invasive magnetic susceptibility monitoring and modelling (MSMM)~~
Magnetic susceptibility monitoring and modelling (MSMM): a non-invasive method for acquiring and modelling exceptionally large datasets from column experiments with manufactured nanoparticles

Michael S. Riley¹ *, Neil Suttie¹, Carl T. Stevenson¹, John H. Tellam¹

¹School of Geography, Earth and Environmental Sciences
University of Birmingham
Edgbaston
Birmingham B15 2TT
UK

*Corresponding Author

Tel: +44 (0)121 414 6139

Fax: +44 (0)121 414 4942

E-mail: M.Riley@bham.ac.uk

ABSTRACT

Identifying and quantifying the processes governing nanoparticle transport in porous media using breakthrough curves with or without retention profiles from laboratory column experiments is frequently subject to uncertainty due to the limited information content of such datasets. An integrated system of automated, non-invasive magnetic susceptibility monitoring and numerical modelling (MSMM) has been developed to provide exceptionally detailed datasets for assessing the validity of transport models of magnetic nanoparticles within a column. MSMM produces the equivalent of a breakthrough curve for each monitored location along the column and uses the enhanced dataset to constrain numerical models more effectively. The results of 2 example column experiments using magnetite nanoparticles ~~and interpreted with MSMM~~ are presented to demonstrate the approach: (i) using quartz sand (with 46,002 susceptibility measurements over 37 hours) and (ii) using crushed Triassic Sandstone (with 19,654 measurements over 20 hours). The quartz sand experiment showed no nanoparticle retention: MSMM showed the system could be well described by an advection-dispersion model, which predicted a breakthrough curve consistent with that derived from magnetic monitoring and with the breakthrough curve acquired independently using a fluorescein tracer. In contrast, no breakthrough was observed in the sandstone experiment, but even in the absence of a breakthrough curve, MSMM indicated that the retention processes were spatially heterogeneous and consistent with a combination of parameterised models of physical straining and limited capacity irreversible attachment.

Keywords

nanoparticle; magnetic susceptibility; column experiment; mathematical model; MSMM

1. INTRODUCTION

The potential environmental impacts of the incidental release of manufactured nanoparticles into aquifers and the wider aquatic environment have been the subject of numerous studies. In addition, the potential risks associated with the use of nano zero-valent iron (nZVI) in subsurface remediation has also been discussed [1], and a voluntary moratorium on the implementation of nanoremediation has been in place in the UK since 2005 [2]. Understanding the transport of manufactured nanoparticles in aquifers is fundamental both to predicting the spread of nanoparticle contamination and to designing safe and effective remediation strategies with nZVI. The processes underpinning nanoparticle transport in aquifers are complex, but might be classified broadly into advection, hydrodynamic dispersion, retention and aggregation. Identification and the quantitative characterization of retention processes present significant challenges to investigators. A range of retention processes has been suggested including physical straining; and primary or secondary minimum attachment [3, 4], which are often assumed to be irreversible or reversible respectively. Typically, empirical kinetic relationships are used to describe each process.

The testing of quantitative models of nanoparticle migration is often based upon breakthrough curves derived from column experiments, sometimes augmented by retention profiles acquired at the end of each experiment. The information content of such data is limited: a breakthrough curve gives nanoparticle concentrations in the carrier fluid over time at a single location in space, and a retention profile gives a spatial distribution of retained nanoparticles at just a single point in time, namely the end of the experiment. As the number of parameters needed to describe the retention processes increases, there is an increasing possibility of non-unique sets of parameter values producing similar fits to the data, resulting in uncertainty in the parameterisation of a conceptual model. Perhaps more significantly, such limited data may be consistent with a number of conceptual models, potentially leading to a fundamental misunderstanding of the processes governing nanoparticle transport. Including measurements taken along the full length of the column throughout an experiment provides the investigator with a record of the temporal evolution of the spatial distribution of nanoparticles, which can potentially reduce the uncertainty in model identification and quantification. Techniques that provide such measurements can be classified broadly as invasive or non-invasive.

Invasive methods for monitoring pollutant transport within porous media, such as repeat sampling from ports along a column, have the disadvantage of affecting the experiment and typically sampling over small, potentially unrepresentative volumes. Additionally, destructive methods of analysing retention profiles, particularly in intact rock, require the column to be sliced, which limits the spatial resolution of data and results in an unquantified loss of nanoparticle mass [5]; and distinguishing nanoparticles retained in a rock from naturally occurring particles can be problematic, e.g. when using iron or silica-based nanoparticles.

Several non-invasive or minimally invasive methods exist including fluorescence imaging [6], scanning optical fibre fluorescence profilers [7], and positron emission projection imaging [8]. Magnetic resonance imaging has the potential to allow the high-resolution, three-dimensional investigation of transport through columns [9], although its use is restricted to media with low concentrations of ferromagnetic substances. None of the above are without disadvantages: a critical review of non-invasive monitoring techniques is given by Werth et al. [10].

We present an investigation method based upon magnetic susceptibility logging (MSL), a non-invasive technique, used routinely in the investigation of the microstratigraphy of rock cores, in which the magnetic susceptibility of slices across a cylinder is measured. MSL been used successfully to image single profiles of nZVI along a column [11, 12] and to produce a manually acquired sequence of profiles during a transport experiment using maghaemite nanoparticles [13]. Naturally occurring iron in the rock can be accounted for simply by taking initial background susceptibility measurements along the column. The accuracy of MSL using industry-standard equipment is well understood [14]. However, the relationship between magnetic susceptibility and the distribution of mass between

nanoparticles suspended in fluid and those retained on the rock needs to be clarified before MSL can be used with confidence in the quantitative modelling of reactive nanoparticle transport. Specifically:

- Restricting the rotational mobility of nanoparticles in suspension can significantly reduce their magnetic susceptibility [15-19]. Thus, nanoparticles retained on the rock surface tend to have a smaller susceptibility compared with similar particles in suspension that are fully free to move. We are unaware of this phenomenon having been included in previous studies.

In addition, the quality of the results obtained from the use of MSL in monitoring and modelling column experiments can be improved by dealing with the following issues:

- The manual application of MSL significantly limits the number of susceptibility profiles for use in modelling.
- The measured magnetic susceptibility at a point in a column is actually a distance-weighted, integrated measurement. The natural approach to analysing the results of an MSL experiment is to post-process the measured susceptibility data by deconvolution to give estimates of actual susceptibility at each point in the column, which can then be simulated numerically [12]. However, the deconvolution approach is generally not error free [20].

We address the issues highlighted above by closely coupling an automated version of MSL with a numerical modelling system. The resulting method of magnetic susceptibility monitoring and modelling (MSMM) facilitates the testing of 1-D transport models applied to column experiments even in ferruginous rocks. MSMM is an automated, non-invasive system that provides multiple susceptibility profiles throughout an experiment. It employs a modelling approach that automatically accounts for the difference in the susceptibility signals attributable to suspended and retained nanoparticles and avoids the need for data deconvolution.

In the following, we demonstrate the use of MSMM in the development and testing of mathematical models of nanoparticle transport derived from experiments with columns containing media with contrasting properties, viz. (i) a clean quartz sand in which nanoparticle retention is insignificant, and (ii) a heterogeneous distribution of crushed Triassic Sandstone in which the retention processes are sufficient to prevent nanoparticle breakthrough within the time frame of the experiment.

2. MODELS OF NANOPARTICLE TRANSPORT

For the purpose of illustration, we consider nanoparticle transport to be describable here in terms of the processes of advection, dispersion, straining, and reversible and irreversible attachment to the rock. Although we do not consider the effects of dual porosity or particle aggregation in this instance, there is no reason why appropriate models could not be applied if necessary. The total mass of particles per unit **bulk** volume of rock is then given by

$$Mass = nC + (1 - n)\rho_S(F_S + F_A + F_R) \quad (1)$$

where n is the porosity [-],
 C is the mass of particles per unit volume of fluid [ML^{-3}],
 ρ_S is the density of the solid material comprising the rock [ML^{-3}],
 F_S is the mass of strained particles per unit mass of rock [-],
 F_A is the mass of irreversibly attached particles per unit mass of rock [-], and
 F_R is the mass of reversibly attached particles per unit mass of rock [-].

Assuming the porosity to be constant in time, the one-dimensional mass balance equation can be written:

$$n \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(nD \frac{\partial C}{\partial x} - nuc \right) - (1-n) \rho_s \left(\frac{\partial F_s}{\partial t} + \frac{\partial F_A}{\partial t} + \frac{\partial F_R}{\partial t} \right) \quad (2)$$

where u is the velocity [LT^{-1}], and
 D is the hydrodynamic dispersion coefficient [L^2T^{-1}].

A wide variety of models has been used to describe the interaction between nanoparticles and the rock [21]. The following are presented simply to illustrate the application of the MSMM technique.

Physical straining is described here by a straining factor, λ [L^{-1}] [3, 22], giving:

$$(1-n) \rho_s \frac{\partial F_s}{\partial t} = \lambda n u C \quad (3)$$

Reversible attachment to the rock is described by:

$$(1-n) \rho_s \frac{\partial F_R}{\partial t} = K_R^{att} \left(1 - \frac{F_R}{F_R^{max}} \right) n C - (1-n) \rho_s K_R^{det} F_R \quad (4)$$

where K_R^{att} is the attachment rate constant [T^{-1}],
 K_R^{det} is the detachment rate constant [T^{-1}], and
 F_R^{max} is the maximum mass of reversibly attached particles per unit mass of rock [-].

Irreversible attachment to the rock is derived from Equation (4) by setting the detachment rate constant to zero and replacing the subscript R by A to denote irreversibility.

3. BACKGROUND THEORY OF NANOPARTICLE MAGNETISM

3.1 Introduction

In Section 3 we outline the theory describing the magnetic behaviour of a class of nanoparticles referred to as *superparamagnetic*, which are fundamental to MSMM. Of particular interest here are magnetite nanoparticles with diameters of around 10 nm. The discussion relates primarily to the property of magnetic susceptibility, its dependence upon nanoparticle numbers, and some issues concerning its measurement. A summary of the principal theoretical results discussed here that underpin MSMM is given in Section 3.9.

3.2 Magnetic susceptibility

When a magnetic field (H) is applied to an object there is a tendency for the constituent material to become magnetized. The (intensity of) *magnetization*, M , is the induced magnetic moment per unit volume.

If the induced magnetization is parallel to the applied field, then the *magnetic susceptibility*, χ [-], is defined by

$$\chi = \frac{dM}{dH} \quad (5)$$

The representation of magnetic susceptibility in Equation (5) is also called the *volume susceptibility* to distinguish it from the *mass susceptibility* and *molar susceptibility*, which are mutually proportional.

3.3 Diamagnetism and paramagnetism

Diamagnetism is a sub-atomic-level property of all materials that gives rise to a negative contribution to the material's total susceptibility. The principal materials in this study that are purely diamagnetic are deionized water, which has a susceptibility of -9.035×10^{-6} at 20°C, and quartz and PVC ([polyvinyl chloride](#)) with susceptibilities of approximately -1.54×10^{-5} [23] and -1×10^{-5} [24] respectively.

Paramagnetic solids exhibit a positive total susceptibility due to a partial realignment of atomic magnetic moments in response to the application of an external magnetic field. Removal of the applied field leads to demagnetization of the solid. Paramagnetic minerals are common in rocks. Biotite, for example, has susceptibility in the range 1.5×10^{-3} to 2.9×10^{-3} [25].

3.4 Ferromagnetism and ferrimagnetism

Ferromagnetic and *ferrimagnetic* nanoparticles have a *spontaneous magnetization*. That is, each particle possesses a magnetization, without the application of an external magnetic field, due to the intrinsic arrangement of the atomic magnetic moments within the particle.

The moments in a ferromagnetic particle are all aligned in the same direction, producing a strong magnetization. Ferromagnetic elements (e.g. iron, cobalt and nickel) are rare in the environment in pure form. Far more common are ferrimagnetic particles (e.g. iron oxides) in which the majority of the moments are aligned in one direction, but the rest are aligned in the opposite direction. Typically, the spontaneous magnetization is anisotropic. The form of the anisotropy can be complex, but there is generally an 'easy' axis of magnetization relative to the particle. This defines two preferential directions of magnetization parallel to the axis, which represent minimum magnetic energy states. The magnitude of the energy barrier between those states depends upon particle size.

3.5 Superparamagnetism

The application of an external magnetic field superposes an additional minimum energy component in the direction of the applied field. The resultant energy distribution has two minima; a primary minimum that tends towards the direction of the applied field with increasing field strength, and a secondary minimum in the opposite direction. For sufficiently small nanoparticles, the thermal energy available at a given temperature can be sufficient to cause the magnetization to switch continuously between the two energy minima. The average time between consecutive states is called the *Néel relaxation time*, τ_N , and is given by

$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \quad (6)$$

where τ_0 is the reciprocal of the frequency of attempts to jump the energy barrier, which is material dependent [T],

K is the magnetic anisotropy energy density [$\text{ML}^{-1}\text{T}^{-2}$],

V is the particle volume [L^3],

k_B is the Boltzmann constant [$\text{ML}^2\text{T}^{-2}\Theta^{-1}$], and

T is the temperature [Θ]

[26].

The argument of the exponential function in Equation (6) is the ratio of the height of the energy barrier separating the energy minima to the available thermal energy.

The exponential dependence of τ_N on V leads to relaxation times ranging between fractions of a nanosecond and many thousands of years. For large ferromagnetic and ferrimagnetic particles, the long relaxation time results in a remanent magnetization that persists when the magnetizing field is removed. However, for sufficiently small particles, the mean magnetization rapidly decays to zero within typical measurement timescales. Such small particles, which have a higher susceptibility than paramagnetic particles, but are similarly incapable of carrying a remanence, are termed *superparamagnetic*.

Magnetite is a ferrimagnetic mineral that has a particularly high susceptibility. Spherical magnetite particles with diameters less than 25-30 nm are often regarded to be superparamagnetic at room temperature [27, 28], although work by others [29, 30] suggests values as low as 17 nm are necessary in some circumstances.

3.6 The susceptibility of superparamagnetic nanoparticles

For a collection of identical, randomly orientated, superparamagnetic nanoparticles, the relationship between the net induced magnetization and the applied field resulting from thermal switching is given by:

$$M = NmL\left(\frac{\mu_0 Hm}{k_B T}\right) \quad (7)$$

where L is the Langevin function:

$$L(x) = \coth(x) - x^{-1} \quad (8)$$

and M is the induced magnetization [$L^{-1}I$],
 N is the particle number density [L^{-3}],
 m is the magnetic moment of each particle [L^2I],
 μ_0 is the permeability of free space [$MLT^{-2}I^{-2}$], and
 H is the strength of the applied magnetic field [$L^{-1}I$]

e.g. Powles [31].

As the applied field increases in strength, the magnetization increases to a limiting value, the *saturation magnetization* (Figure 1). For weak applied fields, which are of interest here, the susceptibility is well approximated by

$$\chi \approx \left. \frac{dM}{dH} \right|_{H \rightarrow 0} = N \frac{\mu_0 m^2}{3k_B T} \quad (9)$$

indicating that the susceptibility is proportional to the particle number density and inversely proportional to the absolute temperature.

3.7 The measured susceptibility of nanoparticles

Typically, measurements of magnetic susceptibility are made by monitoring the magnetic response of an object to an alternating magnetic field. The measured susceptibility, χ' , of a superparamagnetic

nanoparticle is related to the angular frequency, ω , of the applied field and the effective relaxation time, τ_{eff} of a particle by

$$\chi' = \chi_{\infty} + \frac{\chi - \chi_{\infty}}{1 + \omega^2 \tau_{eff}^2} \quad (10)$$

where χ is given by Equation (9) and χ_{∞} is the stable, limiting value of the measured susceptibility with increasing frequency, given by

$$\chi_{\infty} = N \frac{\mu_0 m^2}{3KV} \quad (11)$$

e.g. Worm [30].

Equation (9) through to Equation (11) indicate that, for weak magnetic fields, the measured susceptibility reduces with relaxation time, and is proportional to the particle number density and partly inversely proportional to temperature. The sensitivity to temperature is not significant under typical changes in room temperature.

3.8 The susceptibility of particles in suspension

For superparamagnetic particles suspended in a fluid, changes in the net magnetization are partially determined by Néel relaxation, as in the case of particles rigidly fixed in space, but are also affected by the rotation of particles due to their Brownian motion. This additional process is characterized by the *Brownian relaxation time*, τ_B , given by

$$\tau_B = \frac{3\eta V_H}{k_B T} \quad (12)$$

where η is the fluid dynamic viscosity [$\text{ML}^{-1}\text{T}^{-1}$], and

V_H is the particle hydrodynamic volume [L^3]

[32, 33].

In this section, we make the simplifying assumption that nanoparticles retained on the rock surface are fixed and not significantly affected by Brownian motion.

The effective relaxation time for particles in suspension [15] is given by

$$\tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B} < \tau_N \quad (13)$$

Equation (13) and Equation (10) together show that, in a given volume of rock, the measured susceptibility of a nanoparticle in suspension is greater than that of a similar nanoparticle retained by the rock.

3.9 Summary of the relevant properties of superparamagnetic particles

- Superparamagnetic nanoparticles have a high susceptibility so can be detected in low concentrations (Section 3.5)
- The susceptibility of nanoparticles is proportional to the number density (Section 3.6 and Section 3.7)
- The susceptibility of nanoparticles is not sensitive to everyday changes in room temperature (Section 3.6 and Section 3.7)
- The susceptibility of individual nanoparticles in suspension is greater than that of those retained on the rock surface (Section 3.7 and Section 3.8)

The first two of the above properties are fundamental if magnetic susceptibility is to be used for measuring nanoparticle concentrations, and the third is convenient. In this paper, we distinguish the proportions of free and retained nanoparticles by mass balance modelling.

4. MATERIALS AND METHODS

4.1 Materials

4.1.1 Experimental rig

An experimental rig was constructed capable of monitoring column experiments automatically with Bartington MS2C and MS2B sensors [34] (Figure 2). The MS2C measures the susceptibility of slices across the column, and the MS2B measures the susceptibility of a known volume of fluid. The rig was built on a wooden frame using non-magnetic materials to maximize the uniformity of the ambient magnetic field.

An experimental column is suspended vertically and counterbalanced by an inactive column. Flow to and from the column is via 1/16" (1.6 mm) id silicon tubing, and is driven by a peristaltic pump. The effluent is routed to a fraction collector taking integrated samples continuously over regular intervals to provide breakthrough curve data.

The experimental column hangs through the middle of a horizontally mounted Bartington MS2C core logging device and is centralized in the 50 mm aperture by a system of brushes. The column is driven vertically by a stepper motor, stopping at spatial intervals of 6.11 mm along the column where susceptibility readings are taken automatically using the core logger. MS2C measurements are effected by applying an alternating magnetic field of frequency 565 Hz and amplitude 250 μ T, which is approximately 5 times the strength of the Earth's magnetic field at the experimental location. This produces a sequence of readings at intervals of approximately 2 s. Once the column has been scanned, it returns automatically to its initial position after which another scan begins. Between scans, a single measurement is taken automatically 15 cm beyond the end of the column in air as a standard to allow correction for instrumental drift.

The magnetic susceptibility of the injected and effluent ferrofluid can be measured manually using a Bartington MS2B dual frequency sensor (465 Hz and 4650 Hz), which accepts 10 ml cylindrical vials of fluid (Figure 2) and has a resolution of 2×10^{-6} [14].

The relationship between the susceptibility measured by the MS2C and underlying susceptibility of the sample in the column depends upon the aperture of the instrument and the diameter of the sample. The ratio of the magnitude of the response of the instrument to a cylinder of diameter d to its true susceptibility is given by

$$f_d = 3.45 \left(\frac{d}{D_C} \right)^3 \quad (14)$$

where D_C is the measurement coil diameter, nominally 8 mm greater than the diameter of the instrument aperture [14].

However, f_d is particularly sensitive to d for the dimensions of the equipment used in the experiments. In addition, although of less significance, the MS2C and MS2B instruments employ slightly different measurement frequencies. Thus, there is a potential problem in accurately relating the measured susceptibility of fluid in the core to that of the influent and effluent suspensions. The approach taken here is to determine empirically the ratio, R , of the susceptibility measured using the MS2C of a sample of fluid contained in an otherwise empty PVC pipe, to the susceptibility of the same fluid measured using the MS2B.

In this experiment the standardizing measurement was taken at the inlet end of the column with the inlet tubing passing through the MS2C logger. Using Equation (14), the fluid in the 1.6 mm diameter tubing has a measured susceptibility reduced from its true value by a factor of approximately 7.2×10^{-5} which, for practical ferrofluid concentrations, gives values orders of magnitude below the range of the sensor. Experiments confirmed that fluids in the tubing of concentrations twice that injected were undetectable.

Control of the motor, susceptibility measurement, and the recording of measurements were achieved using a Raspberry Pi computer.

4.1.2 Rock columns

The results of two experiments are presented here. The experimental columns comprised 40 mm od, 34 mm id clear PVC pipes of different lengths. Experiment 1 was conducted in a pipe filled with clean, fine-medium grained quartz sand (dried industrial sand). Experiment 2 was conducted in a pipe filled with sandstone aggregates (sizes predominately between 0.5 mm and 1 mm), created by crushing two samples of English Triassic Sherwood Sandstone Group; haematite coated, carbonate cemented, fine-medium grained continental, mainly quartz sandstone containing feldspar, clays, and biotite [35]. Sediment samples were used in the experiments without further treatment.

In both experiments, a holed rubber bung was fitted in the pipe with a Nitex 100 micron nylon filter screen covering the inside of the bung. The pipe was held vertically, filled with water and the sample material was gradually added while the tube was gently agitated. When full, a filter and rubber bung was fitted to the top of the pipe. The weight of all components was measured to allow a porosity calculation to be made.

4.1.3 Nanoparticles

The nanoparticles used were Ferrotec EMG705 magnetite (Fe_3O_4) supplied as a 3.9% by volume suspension in deionized water with an anionic surfactant. TEM images (e.g. Figure 3) indicate particle diameters to be normally distributed with mean 12.12 nm and standard deviation 3.38 nm.

Nanoparticle suspensions were made up by diluting the stock suspension with deionized water. The resulting concentrations and mean nearest neighbour inter-particle distances (calculated using the method of Tournos [36]) are given in Table 1. All suspensions were left in an open flask to equilibrate with the laboratory atmosphere for two days and then sonicated for 30 minutes before use.

Suspensions were found to be effectively stable in terms of mean particle size and magnetic response. A time series of dynamic light scattering measurements on the more concentrated suspension

(100 mg l⁻¹) using a Malvern Instruments Zetasizer Nano ZS over a period of 74 hours indicated an increase in hydrodynamic diameter of less than 0.06% of the DLS estimated mean particle diameter per hour. Independent experiments indicated that a similar suspension of nanoparticles in deionized water showed no significant change in the measured magnetic susceptibility for several days longer than the experiments reported here.

4.1.4 Experimental procedure

In the experiments described here, nanoparticle suspensions were made up with deionized water. However, more generally, a carrier fluid with a chemistry appropriate to a particular field situation might be required. In general, the pumping sequence would be: deionized water to remove potentially mobile natural colloids that might facilitate nanoparticle transport; water with the appropriate chemistry to prime the column and achieve a steady background susceptibility; a nanoparticle suspension; and water with the appropriate chemistry to flush the column fluid and remove any reversibly retained nanoparticles remaining in the column. A final flush with deionized water might be valuable under some circumstances.

Table 1 summarises key parameters characterising the experiments presented.

Parameter	Units	Experiment 1	Experiment 2
Length of column	m	0.40	0.22
Rock sample	-	Clean quartz sand	Crushed Triassic Sandstone
Gravimetric porosity estimate	-	0.281	0.32
Flow rate	ml s ⁻¹	2.9×10 ⁻³	1.2×10 ⁻²
Duration of injection	hours (PV)	24.7 (~25.4)	7 (~4.7)
Duration of flush	hours (PV)	12.1 (~12.4)	13 (~8.8)
Injected fluid concentration	mg l ⁻¹	100	20
Injected fluid susceptibility (MS2C)	-	5.63×10 ⁻⁴	1.14×10 ⁻⁴
Mean inter-particle distance	nm	201	344
Number of scans during injection	-	434	221
Number of scans during flush	-	263	413
Number of susceptibility measurements in the column	-	46,002	19,654

Table 1: Summary of parameters for each experiment described. Times are reported in hours and pore volumes (PV).

Following Experiment 1 a fluorescein tracer test was conducted in the column using the same test rig and plumbing. Fluorescein was sampled using the fraction collector and analysed off-line.

4.2 Modelling strategy

The purpose of modelling the experiments is to test models of nanoparticle migration. The mathematical models considered here are outlined in Equation (2) through to Equation (4). The state variables are related to the magnetic susceptibility, χ , due to particle transport by

$$\chi = \gamma[nC + \theta(1-n)\rho_s(F_s + F_R + F_A)] \quad (15)$$

where γ is the susceptibility per unit mass of particles in a unit volume of column [$M^{-1}L^3$], and θ is the ratio of the susceptibility of a particle attached to the rock to the susceptibility of a similar particle in suspension [-] and is assumed to be constant and independent of the retention process.

Setting $\gamma = 1$ results in simulations with nanoparticle masses per unit volume of column expressed as equivalent susceptibilities, which is the approach adopted here.

In experiments that exhibit nanoparticle retention, the parameter θ controls the overall mass balance, and is estimated under the conditions prevailing during a column experiment. This approach is necessitated by the results of preliminary experiments in which nanoparticles were immobilised either in a gel or by freezing, giving values of θ of 0.72 and 0.33 respectively, indicating the potential importance of the mode of immobilisation.

To avoid the need to post-process the experimental data by deconvolution, aspects of the monitoring are also modelled. A measurement made with the MS2C device is effectively an integrated set of measurements taken over distances either side of the measuring coil. The contribution to the overall measured value of a thin section of the column at a displacement L from the centre of the coil can be characterized by an empirically-derived instrument response function $g(L)$, such that

$$\int_{-\infty}^{\infty} g(L) dL = 1 \quad (16)$$

Thus, measured values of susceptibility are convolutions of the actual values with the instrument response function.

The overall approach to modelling is to:

- simulate nanoparticle transport in the column;
- apply a correction for the column diameter and the difference in frequencies of the MS2C and MS2B (Section 4.1.1.);
- perform a numerical convolution of the model results with the instrument response function, to simulate the measured susceptibilities; and
- estimate the transport parameters by comparing simulated measurements with experimental results.

More formally, the model error at location x , measured from the inlet end of the sand column, is given by

$$\varepsilon(x) = R \int_{-\infty}^{\infty} \chi(\xi) g(x - \xi) d\xi - [\chi'(x) - \chi'_{init}(x)] \quad (17)$$

where $\chi'(x)$ represents the measurements taken during the injection and flushing of nanoparticles, and $\chi'_{init}(x)$ is the measured background susceptibility.

Following initial flushing with deionized water, susceptibility profiles of each column were taken and averaged to give an estimate of the background susceptibility. The profiles included measurements taken beyond the inlet end of the column. These additional measurements were used with measurements from the first 0.15 m of the column used in Experiment 2 to fit an instrument response function, given by a normal distribution with a standard deviation, σ , of 0.0141 m, with an RMS error of 2.26×10^{-7} (Figure 4a). This result is supported by functions derived independently using fluid filled columns that gave $\sigma = 0.0140$ m and $\sigma = 0.0149$ m.

The background in Experiment 2 shows an unexpectedly large, variable reduction towards the outlet end. This cause of this reduction is uncertain. Given the uncertainty in characterizing this region, the 5 measurements nearest the outlet end of the column were not included in model fitting. Figure 4b shows the background measurements for Experiment 1 with the instrument response function derived from the injection phase of Experiment 2.

All calculations were carried out in MATLAB (MathWorks). The ~~finite difference~~ grid size for numerical calculations was determined by refining the monitoring interval by increasing powers of 2 until the consequent changes in the solution were negligible. The calculations presented here were achieved with refinement by a factor of 16, giving a grid size of 3.82×10^{-4} m. Output times were specified to match the experimental monitoring. Calculation time steps were determined automatically by the *pdepe* routine in MATLAB. Convolution calculations were achieved using an extended integration formula [20] based upon the refined grid. Goodness of fit to the data was evaluated using the RMS of the error shown in Equation (17). Automated model fitting was achieved using the optimization routine, *fmincon*.

It is convenient to represent the data as a time series of susceptibility profiles (e.g. Figure 5). Consequently, for presentation purposes, data values at each measurement location have been linearly interpolated between actual measurement times to give values at regular time intervals. Model fitting was carried out solely on the raw data.

5. RESULTS

5.1 Experiment 1

Figure 5 shows samples of the 697 profiles measured above background during the early injection and the flushing phases of the experiment. Measurements close to the ends of the column show reduced values due to the proximity of the regions beyond the ends of the column, which have zero susceptibility. The profiles exhibit plateaux that vary along the column, but show a consistent structure over time. This variability is almost certainly due to porosity variations along the column: the measured susceptibility is particularly sensitive to porosity in this experiment due to the strong contrast between the susceptibility of the magnetite suspension and that of the sand in the column. An accurate calculation of the porosity variation from the data is not straightforward since susceptibility measurements represent actual susceptibility values integrated over distance. However, a rough estimate can be established by ignoring the convolution effect of the measurement and assuming the sand to have a uniform susceptibility typical of quartz. This approach suggests the full range of porosity variation inferred from the data to be around 2.7%.

No nanoparticle retention was observed in the first 22 hours of the experiment. For 2 hours during the injection phase starting at 1360 minutes (i.e. after the column was fully flooded with nanoparticles), the discharge was trebled to encourage physical straining, but nothing significant was observed.

The full dataset from within the column can be modelled well by a simple one-dimensional advection-dispersion model with homogeneous parameters, using the measured porosity of 28.1% as the effective porosity and with a manually fitted dispersivity of 0.0015 m (Figure 5). Optimised values of porosity and dispersivity were essentially the same at 28.07% and 0.0015 m respectively, with an RMS error of 5.9×10^{-6} . A movie of the full experimental data, the best fit measurement model, and the inferred underlying nanoparticle concentrations in each phase expressed in terms of equivalent magnetic susceptibility, are given in Figure S1.

Figure 5 (b) indicates slightly elevated susceptibility measurements close to the inlet end of the column. Deconstruction of similar columns indicates discolouration of the 100 micron filter screen at the injection pipe due to permanent particle attachment, which is the likely cause.

The model inferred from the column data was used to predict the breakthrough curve measured using the fraction collector and the MS2B dual frequency sensor (Figure 6). Each sample was collected over a period of one hour. Mass recovery measured in terms of magnetic susceptibility was calculated to be 100% (to the nearest percent). A partial fluorescein breakthrough is shown with open green circles, which agrees well with the susceptibility data.

5.2 Experiment 2

5.2.1 Overview

Figure 7(a) shows 6 profiles of the spatial distribution of susceptibility above background at 70 minute intervals during the nanoparticle injection phase of the experiment.

Figure 7(b) shows the final profile presented in Figure 7(a) (indicated by measurements joined with a solid line) and a second profile taken 70 minutes into the period of flushing with deionized water. The temporal reduction in susceptibility in the first part of the column is due to the removal of the particles in suspension due to the flushing. The increase in susceptibility towards the outlet end of the column is due to the continuing retention of particles as they are flushed from the inlet end. The subsequent 369 profiles are effectively unchanging during the remainder of the experiment, over which time the mean standard deviation of the measurements at each location was 9.46×10^{-7} and the maximum standard deviation was 1.3×10^{-6} (Figure 8). Thus, the profile in Figure 8 represents the mean magnetic susceptibility measurements obtained from the retention profile.

The full set of results is shown as a movie in Figure S2.

5.2.2 Identification of an initial conceptual model

The detail and quality of the data obtained using MSMM can provide insights into (i) the nature of the retention processes operating in the column and (ii) the heterogeneity of the sediment in the column, using simple observations prior to numerical modelling.

Figure 8 implies that retention, which is effectively total, is dominated by processes that are irreversible, at least on the time scale of the experiment. Additional evidence suggesting the form of the retention processes can be extracted from Figure 7 and Figure S2, which show the rate of change of the peak value of susceptibility reducing with time to an effectively constant value. These observations suggest the possibility that retention is governed by two processes: one that proceeds at a steady rate, such as straining as described by Equation (2); and another in which the rate of retention tends to zero with time, such as reversible or irreversible attachment with a limited capacity as described, for example, by Equation (4) or an appropriately modified version of Equation (4) respectively.

Figure 7, Figure S2 and Figure 8 show an unexpected hump in the profiles at approximately 8 cm along the column. Plots of the logarithm of the susceptibility measurements with distance from the

initial peak onwards show two straight lines. The location of the intersection of these lines does not change with time, suggesting a change in rock property around that location. We hypothesise here that the transport properties change at a certain point in the column producing two effectively homogeneous regions with potentially distinct properties. The heterogeneity is almost certainly due to the preparation of the contents of the column, which was carried out in batches for this experiment.

5.2.3 Numerical modelling results

~~Reversible attachment was not simulated since the data indicate the predominance of irreversible retention processes.~~ For the purposes of demonstration, simulations were carried out using a combined model of straining and irreversible attachment. The measured porosity of 0.32 was used throughout the simulations. The solids in the sandstone are mainly quartz with an assumed density of $2.65 \times 10^3 \text{ kg m}^{-3}$.

To account for the hypothesised spatial heterogeneity, the column was divided conceptually at $x = 0.075 \text{ m}$ into two regions with distinct parameter values. Varying the porosity between the two regions was found to have little effect on the results. The straining factor, λ , and the irreversible attachment rate constant, K_A^{att} , were considered individually and jointly to vary spatially.

Model calibration was achieved by optimizing the parameters in Table 2 using that part of the dataset covering the period in which measured values continue to change significantly; nominally the first 500 minutes (265 profiles). Subsets of the best fit modelling results are displayed in Figure 7, and in full as a movie in Figure S2. The relative contributions of the constituent transport processes are shown for the end of the injection phase and in steady state during the flushing phase in Figure 9 and over the full simulation in Figure S2. The shapes of the profiles in this experiment are dominated by the retention processes and, consequently, the optimized parameter values in Table 2 are not sensitive to changes in dispersivity. For example, fixing the dispersivity at 0.001 m and optimizing the remaining parameters resulted in typical changes in the optimized parameters of approximately 1%.

Parameter	Units	Optimised values
<u>α</u>	<u>m</u>	<u>1.50×10^{-3}</u>
λ ($x < 0.075 \text{ m}$)	m^{-1}	7.22
λ ($x > 0.075 \text{ m}$)	m^{-1}	9.42
K_A^{att} ($x < 0.075 \text{ m}$)	s^{-1}	1.61×10^{-7}
K_A^{att} ($x > 0.075 \text{ m}$)	s^{-1}	2.45×10^{-7}
F_A^{max}	-	1.83×10^{-7}
θ	-	6.50×10^{-1}
RMS error	-	4.32×10^{-6}
Mean error	-	-3.24×10^{-7}

Table 2: Calibrated parameter values, RMS and mean errors (given to 3 significant figures) based upon the assumptions of heterogeneous K_A^{att} and heterogeneous λ .

Additional simulations confirmed that both assumed retention processes were required to reproduce the magnetic susceptibility measurements.

6. OBSERVATIONS AND COMMENTS

6.1 Errors and the injection system

The largest errors in the model fit in both experiments occur close to the inlet following a change in injected fluid. In these experiments, both inlet and outlet consist simply of a narrow tube separated from the sediment in the column by a nylon mesh. Consequently, neither flow nor transport close to the ends of the column is truly one-dimensional and, in particular, flooding the full width of the column with the new fluid is not instantaneous as would be required by a one-dimensional model. Thus, a one-dimensional advection-dispersion model that has been parameterised using the full dataset will overestimate the susceptibility near the injection end of the column during the early stages of nanoparticle injection, and underestimate the susceptibility as the flushing phase begins. This is seen clearly in Experiment 1 (Figure 5). In systems with nanoparticle retention, the exact magnitude and spatiotemporal extent of the error is determined partially by the kinetics of the retention processes and so the effect of the injection system is more difficult to predict. Nevertheless, in Experiment 2, there is also an initial overestimate of the susceptibility close to the inlet in the first 30 minutes following nanoparticle injection (Figure S1). Although the effect of an alternative injection system might be predicted by modelling in 2 or 3 dimensions, the use of MSMM could provide a useful test of such a system based directly upon measurement.

6.2 The susceptibility of suspended and retained particles

In Experiment 2, the optimized value of θ was found to be particularly stable for a variety of assumptions regarding the heterogeneity of the retention processes since its estimation is governed simply by mass balance considerations. The estimated magnitude of θ (0.65) highlights the importance of distinguishing between the measured susceptibility of suspended and retained particles. As noted in Section 3.8, the reduction in Brownian rotation of nanoparticles with limited mobility causes a reduction in susceptibility. Additional mechanisms that could have a similar effect are the subject of current magnetic nanoparticle research. A fully quantitative understanding of such phenomena would be valuable in exploring the possibility and potential utility of a dependence of θ upon the nature of the immobilisation process.

6.3 Complexity

The effective use of MSMM in the quantitative characterisation of a simple transport system in which there is no evidence of particle retention or dual porosity effects has been demonstrated (Experiment 1). As expected, MSMM maintains an excellent mass balance. The breakthrough curve predicted from the advection-dispersion model derived from MSMM matches the breakthrough curves measured directly using independent magnetic susceptibility and fluorescein measurements. All breakthrough curves are consistent with an effective porosity that is in excellent agreement with the gravimetrically-derived estimate of bulk porosity. MSMM-derived profiles show that, with the exception of the first few minutes (see Section 6.1 for discussion) the simple advection-dispersion model applies throughout the experiment.

Analysis of the results of Experiment 2 demonstrates the potential value of data obtained using MSMM in the identification and parameterisation of a more complex set of transport processes, even in the absence of a breakthrough curve. The RMS error and bias are just 3.8% and -0.28% of the MS2C-measured injection susceptibility respectively, and visually the model results reflect the principal features of the data, particularly after the early time data, which are influenced by the injection system. It is perhaps worth noting here, that MSMM is a potentially powerful tool in understanding nanoparticle migration quantitatively, but that the choice of processes to include at the modelling stage should also take into account any additional evidence available, e.g. from batch experiments or particle size monitoring.

6.4 Heterogeneity

Typically, column experiments are analysed by fitting a simple one-dimensional numerical model to the experimental results. The effectiveness of this approach depends upon the homogeneity of the column. In natural samples, homogeneity can be problematic. For example, in columns of intact sedimentary rock the presence of stratification or lamination can introduce heterogeneous transport property distributions. A common approach is to run experiments at right angles to the strata where possible. This tends to lead to breakthrough curves that can be modelled by a set of effective parameters, but lack usable information on the distribution of parameter values in each section of the column. Experiments conducted parallel to strata or laminations tend to result in more complex breakthrough curves that can be difficult to model convincingly, e.g. Bashar & Tellam [8]. MSMM uses measurements that are integrated across the column and so cannot completely resolve the problems that might arise from running experiments parallel to laminations. However, it has been employed to identify a discrete property change along a column and investigate the underlying distribution of transport parameter values (Experiment 2). More property zones might be included simply, but care must be taken with the interpretation as the number of parameter values increases. In principle, continuous property variation along the length of the column characterised by a simple function could also be accommodated.

Under favourable circumstances, background susceptibility measurements can provide information about the heterogeneity of the porosity of the column that could be incorporated in the modelling if it were thought to be necessary.

6.5 Further implications

The work reported here uses purely magnetic nanoparticles. However, nanoparticles with a magnetite core covered by shells of other materials are now commonplace in medical applications. So, the surface properties of nanoparticles with a magnetite core can be engineered to reflect the behaviour of other materials. The inclusion of an intermediate silica shell can reduce the magnetic interactions between particles effectively to zero [37]. Consequently, it is expected that MSMM could form the basis for investigating the transport properties of a wide range of metal oxide nanoparticles by utilizing appropriate core-shell nanoparticles.

ACKNOWLEDGEMENTS

This work was supported by the UK Engineering and Physical Sciences Research Council [grant number EP/J017612/1].

The authors wish to thank Clare Walker, Richard Parkinson, Finlay Campbell, and Yifei Gu, who conducted masters-level projects between 2013 and 2015 at the University of Birmingham that helped develop the practical understanding underpinning the project. We also wish to thank Damian Ulbricht of GFZ Potsdam for help in developing the control software; Fraser McNeil-Watson of Malvern Instruments for the use of the Zetasizer; and Michael Fay at the Nanoscale and Microscale Research Centre at the University of Nottingham for the TEM imaging.

REFERENCES

1. Grieger, K.D., et al., *Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: Risk mitigation or trade-off?* Journal of Contaminant Hydrology, 2010. **118**: p. 165-183.
2. Mildowski, R. and J. Wentworth, *Risk Assessment of Nanomaterials*. 2017, Parliamentary Office of Science & Technology, POSTNOTE 562.
3. Bradford, S.A., et al., *Modeling Colloid Attachment, Straining, and Exclusion in Saturated Porous Media*. Environmental Science & Technology, 2003. **37**: p. 2242-2250.
4. Bradford, S.A., et al., *Physical factors affecting the transport and fate of colloids in saturated porous media*. Water Resources Research, 2002. **38**(12).
5. Neukum, C., A. Braun, and R. Azzam, *Transport of stabilized engineered silver (Ag) nanoparticles through porous sandstones*. Journal of Contaminant Hydrology, 20014. **158**: p. 1-13.
6. Bridge, J.W., S.A. Banwart, and A.L. Heathwaite, *Noninvasive quantitative measurement of colloid transport in mesoscale porous media using time lapse fluorescence imaging*. Environmental Science & Technology, 2006. **40**(19): p. 5930-5936.
7. Shang, J., et al., *In-Situ Measurements of Engineered Nanoporous Particle Transport in Saturated Porous Media*. Environmental Science & Technology, 2010. **44**(21): p. 8190-8195.
8. Bashar, K. and J.H. Tellam, *Non-reactive solute movement through saturated laboratory samples of undisturbed stratified sandstone*, in *Fluid Flow and Solute Movement in Sandstones: The Onshore UK Permo-Triassic Red Bed Sequence*, R.D. Barker and J.H. Tellam, Editors. 2006. p. 233-251.
9. Lakshmanan, S., et al., *Characterization of nanoparticle transport through quartz and dolomite gravels by magnetic resonance imaging*. International Journal of Environmental Science and Technology, 2015. **12**(10): p. 3373-3384.
10. Werth, C.J., et al., *A review of non-invasive imaging methods and applications in contaminant hydrogeology research*. Journal of Contaminant Hydrology, 2010. **113**(1-4): p. 1-24.
11. Dalla Vecchia, E., M. Luna, and R. Sethi, *Transport in Porous Media of Highly Concentrated Iron Micro- and Nanoparticles in the Presence of Xanthan Gum*. Environmental Science & Technology, 2009. **43**(23): p. 8942-8947.
12. Tosco, T. and R. Sethi, *Transport of Non-Newtonian Suspensions of Highly Concentrated Micro- And Nanoscale Iron Particles in Porous Media: A Modeling Approach*. Environmental Science & Technology, 2010. **44**(23): p. 9062-9068.
13. Khan, S., D.K. Potter, and E. Kuru, *Quantifying the Transport of Superparamagnetic Nanoparticles in Porous Media Using an Acrylic Flow Cell and Integrated Magnetic Susceptibility Sensor Technique*. Transport in Porous Media, 2015. **106**(3): p. 691-705.
14. Bartington Instruments, *Operation Manual for MS2 Magnetic Susceptibility System. OM0408, issue 48*. n.d., Bartington Instruments Ltd., Oxford, OX28 4GE, UK.
15. Scaife, B.K.P., *On the low-field, low-frequency susceptibility of magnetic fluids*. Journal of Physics D: Applied Physics, 1986. **19**: p. L195-L197.
16. van Berkum, S., et al., *Frequency-Dependent Magnetic Susceptibility of Magnetite and Cobalt Ferrite Nanoparticles Embedded in PAA Hydrogel*. International Journal of Molecular Sciences, 2013. **14**: p. 10162-10177.
17. Shah, S.A., et al., *Mixed Brownian alignment and Néel rotations in superparamagnetic iron oxide nanoparticle suspensions driven by an ac field*. Physical Review B, 2015. **92**.
18. Ota, S., et al., *Rotation of magnetization derived from Brownian relaxation in magnetic fluids of different viscosity evaluated by dynamic hysteresis measurements over a wide frequency range*. nanomaterials, 2016. **6**(170).
19. Wisotzki, E.I., et al., *Magnetic response of gelatin ferrogels across the sol-gel transition: the influence of high energy crosslinking on thermal stability*. Soft Matter, 2016. **12**.
20. Press, W.H., et al., *Numerical Recipes in C: The Art of Scientific Computing*. 2 ed. 1992, Equation 4.1.14: Cambridge University Press.

21. Babakhani, P., et al., *Continuum-based models and concepts for the transport of nanoparticles in saturated porous media: A state-of-the-science review*. Advances in Colloid and Interface Science, 2017. **246**: p. 75-104.
22. Ibaraki, M. and E.A. Sudicky, *Colloid-facilitated contaminant transport in discretely fractured porous media: 1. Numerical formulation and sensitivity analysis*. Water Resources Research, 1995. **31**(12): p. 2945-2960.
23. Dearing, J., *Environmental Magnetic Susceptibility: Using the Bartington MS2 System*. 1999.
24. Wapler, M.C., et al., *Magnetic properties of materials for MR engineering, micro-MR and beyond*. Journal of Magnetic Resonance, 2014. **242**: p. 233-242.
25. Hunt, C.P. and B.P. Moskowitz, *Magnetic properties of rocks and minerals*, in *Rock Physics and Phase Relations: A Handbook of Physical Constants*, T.J. Ahrens, Editor. 1995, American Geophysical Union: Washington, DC, USA. p. 189-204.
26. Néel, L., *Théorie du trainage magnétique des ferrimagnétiques en grains fins avec applications aux terres cuites*. Ann. Géophys., 1949. **5**: p. 99-136.
27. Dunlop, D.J., *Superparamagnetic and single-domain threshold sizes in magnetite*. Journal of Geophysical Research, 1973. **78**(11): p. 1780-1793.
28. Krishnan, K.M., et al., *Nanomagnetism and spin electronics: materials, microstructure and novel properties*. Journal of Materials Science, 2006. **41**(3): p. 793-815.
29. Hrouda, F., *Models of frequency-dependent susceptibility of rocks and soils revisited and broadened*. Geophysical Journal International, 2011. **187**: p. 1259-1269.
30. Worm, H.-U., *On the superparamagnetic-stable single domain transition for magnetite, and frequency dependence of susceptibility*. Geophysical Journal International, 1998. **133**: p. 201-206.
31. Powles, J.G., *Particles and Their Interactions*. International edition ed. 1968: Addison-Wesley Educational Publishers Inc. 272.
32. Debye, P.J.W., *Polar Molecules*. 1929, New York: Chemical Catalog Company. 172.
33. Fannin, P.C. and S.W. Charles, *The effect of particle concentration on the frequency-dependent susceptibility of ferrofluids*. Journal of Physics D: Applied Physics, 1989. **22**: p. 449-450.
34. Bartington Instruments, *MS2/MS3 Magnetic Susceptibility Sysytem*. n.d., Bartington Instruments Ltd., Oxford, OX28 4GE, UK.
35. Tellam, J.H. and R.D. Barker, *Towards prediction of saturated-zone pollutant movement in groundwaters in fractured permeable-matrix aquifers: the case of the UK Permo-Triassic sandstones*, in *Fluid Flow and Solute Movement in Sandstones: The Onshore UK Permo-Triassic Red Bed Sequence*, R.D. Barker and J.H. Tellam, Editors. 2006. p. 1-48.
36. Tournos, F., *Random nanoparticle deposition: inter-particle distances in 2D, 3D, and multilayer samples*. J Nanopart Res, 2011. **13**: p. 5211-5223.
37. Perez, N., et al., *Aggregation state and magnetic properties of magnetite nanoparticles controlled by an optimized silica coating*. Journal of Applied Physics, 2017. **121**(4).

Figure Captions

Figure 1: Non-dimensional graphical representation of net particle magnetization (M) as a function of the applied field (H) with linear approximation for weak fields.

Figure 2: Schematic diagram of experimental rig with photographs of the MS2C core logging sensor and MS2B dual frequency sensor. The controlling computer and the wooden support frame are not shown. The rig is approximately 2 metres tall.

Figure 3: Sample TEM image of Ferrotec EMG705 magnetite nanoparticles used in the experiments. The inset shows the size distribution of 265 manually measured nanoparticles (black dots) and the best fit cumulative normal distribution (red line).

Figure 4: Background susceptibility profiles.

- (a) Mean of 5 measurements of the susceptibility of the column used in Experiment 2 following the initial flushing with deionized water (filled blue circles). Best fit model of susceptibility at the inlet end and central section of the column (red line). Predicted susceptibility at the outlet end of the column (green line). ~~The extent of the column is shown in brown.~~
- (b) Mean of 3 measurements of background susceptibility of the column used in Experiment 1 with the instrument response function shown in (a).

The extent of each column is shown in brown.

Figure 5: A sample of magnetic susceptibility profiles above background from Experiment 1 (solid blue circles) and the corresponding best fit profiles (red lines) taken at 70 minute intervals:

(a) during the early injection phase and

(b) during the flushing phase.

The temporal sequence of profiles runs from left to right in both figures.

Figure 6: Breakthrough curves (Experiment 1) standardised by the injection susceptibility or concentration as appropriate. Red line: predicted breakthrough curve derived from fitting susceptibility data from within the column. Solid blue circles: magnetic susceptibility. Open green circles: fluorescein.

Figure 7: A sample of magnetic susceptibility profiles above background from Experiment 2 (solid blue circles) and the corresponding best fit profiles (red lines) taken at 70 minute intervals (a) during the injection phase and (b) immediately prior to the flushing phase and 70 minutes later. The solid blue line represents the same profile in both graphs.

The temporal sequence of profiles in (a) is indicated by increasing susceptibility. In (b) the profile shown with the solid blue line precedes that shown with the dashed blue line.

Figure 8: Mean ~~retention profile~~ magnetic susceptibility measurements above background averaged over the final 369 profiles measured in the experiment. The mean measured susceptibility is shown by red crosses. The error bars (black) represent ± 3 standard deviations of the measurements at each location.

Figure 9: Measured susceptibility profile and MSMM-inferred susceptibility profiles (a) at the end of the injection period (420 minutes); and (b) at steady state during the flushing phase (510 minutes).

Blue crosses represent measured values of susceptibility above background (interpolated in time) and the red line gives the model fit to the data. The remaining lines show modelled values of the components of the actual susceptibility. Blue: total susceptibility of retained particles; Yellow: irreversibly attached phase. Brown: strained phase. Green: fluid phase.

Supplementary Material Figure Captions

Figure S1: Measured susceptibility profiles and MSMM-inferred susceptibility profiles (Experiment 1).

Blue crosses represent measured values of susceptibility above background (interpolated in time) and the red line gives the model fit to the data. The green line shows the modelled fluid phase component of the underlying susceptibility.

Figure S2: Measured susceptibility profiles and MSMM-inferred susceptibility profiles (Experiment 2).

Blue crosses represent measured values of susceptibility above background (interpolated in time) and the red line gives the model fit to the data. The remaining lines show modelled values of the components of the underlying susceptibility. Blue: total susceptibility of retained particles; Yellow: irreversibly attached phase. Brown: strained phase. Green: fluid phase.